TRACE ELEMENT REDUCTION IN FILTERED COAL EXTRACT SOLUTIONS USING SOLVENT PRECIPITATION

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INTRODUCTION

In two-stage coal liquefaction processes the coal is digested in a solvent in the first stage and then hydrocracked in the second stage in order to increase the hydrogen to carbon ratio and the yield of distillate material. At some point in the process mineral matter and undissolved residual material must be removed, and the processes used for this step are usually filtration or solvent deashing, with the latter taking the form of anti-solvent or critical solvent deashing. The deashing step can occur either between the first and second stages or after the second stage [1]. The major advantage of deashing before the second stage is that it reduces catalyst deactivation during hydrocracking due to both carbon deposition and trace element deposition as reported by Stohl and Stephens[1]. However, even when deashing occurs before the second stage, deactivation of the catalyst still occurs due to both carbon and trace element deposition [1-6]. In the case of carbon deposition the cause is not known, although there is some evidence linking high molecular weight species to carbon deposition [1,7]. With trace elements none of the deashing processes in use is completely effective and, therefore, some trace elements go forward to the hydrocracking stage.

The British Coal process is a two-stage process with filtration as the deashing step occuring between the digestion and hydrocracking stages [8]. Previous work in this laboratory using Point of Ayr and Calverton coals [9,10] has shown that increasing the digestion pressure considerably reduces the ash level in the extract solution after filtration, and that where this effect is modified by the use of different coals or hydrogen-donating solutions, then this can be overcome by reducing the filtration temperature. It was also shown that the distribution of trace elements in the original coal ash was different from that in the extract solution ash. For example, the proportions of manganese and titanium increased twenty-fold and ten-fold respectively, and the proportions of calcium and magnesium also increased. These elements, which show an increase in proportion, have also been found to be catalyst deactivators [11-16] and were also found to deposit most readily on the hydrocracking catalyst [2]. Thus, it is important that the level of these trace elements is as low as possible if their deposition on the hydrocracking catalyst is to be reduced.

Previous work [17,18] studying the form of the trace elements remaining in the filtered coal extract solution shows that their removal is no easy matter. They pass through fine filters and are

not easily removed by guard beds [19]. Increasing the digestion pressure, as described above, has been successful, but efforts to reproduce this effect at low digestion pressures, by the addition of low-boiling material prior to filtration, were unsuccessful [10]. However, it has been shown [18] that the insoluble portion of solvent extractions, used to characterise the filtered coal extract solution, contain a high proportion of the trace elements present in the original extract. The solvents used were pentane, toluene and THF, and with toluene, for example, about 80% of the trace element content precipitated out with the insolubles. Thus, it may be possible to carry out a solvent precipitation on coal extract solution which has already been filtered, in order to reduce the trace element concentration to a very low level.

In this paper work carried out using toluene and THF to remove trace elements from filtered coal extract solutions will be described. The effect of extract to solvent ratio was studied as well as the temperature of extraction. Trace element concentrations have been measured both before and after precipitation, and the nature of the extract solution after solvent precipitation, compared to that of the original extract solution, has been examined.

EXPERIMENTAL

Materials

The coal used was Point of Ayr , supplied by British Coal, preground to -200 µm. An analysis of the coal is given in Table 1. The solvent used in the digestion was process-derived hydrogenated anthracene oil (HAO), again supplied by British Coal.

Procedures

Liquefaction was carried out by heating a mixture of the coal and HAO to a temperature of 400-420°C in a 2 litre autoclave. The pressure was controlled by venting vapours, as required, to a condensing trap. At the end of the digestion period, which was 45 minutes above 400°C, the contents were cooled to the filtration temperature and vapours vented to reduce the pressure to the filtration pressure. The mixture in the autoclave was then filtered through a pressure filter containing a "Nomex" cloth using the residual pressure in the autoclave. A solvent-to-coal ratio of 2:1 was used. The procedure has been described previously [7].

Solvent precipitation experiments were carried out on the filtered extract solution, produced as described above, using a stirred 0.2 litre autoclave. The extract and solvent were mixed together cold, in the autoclave, and then heated to the extraction temperature in a fluidised sand bath. The mixture was agitated at the extraction temperature for 20 minutes and then filtered, using the pressure in the autoclave or an applied nitrogen pressure, into a pressure filter containing a "Nomex" cloth at the extraction temperature. Some experiments were also carried out where the solvent was injected, using an applied nitrogen pressure, into the autoclave

containing the extract at the required temperature.

Analysis

Ash yields of the liquid products were determined by evaporating a sample (≈25 g) in a platinum crucible until coke formed. The ashing was completed in a muffle furnace set at 850°C.

Trace element analysis was carried out on the ash by carrying out a fusion with lithium metaborate followed by dissolution in 10% hydrochloric acid. The resulting solution was analysed using atomic emission and absorption spectrometry (AA). The method has been described previuosly [7].

Analysis was carried out on the fractions which boiled below 350°C of the extract and the filtrate produced after solvent precipitation, using a Perkin Elmer model 8500 GC fitted with a wide-bore, OV-1 capillary column 25 m long and 0.53 µm diameter. The oven temperature was 40°C for 1 minute followed by a temperature ramp at 4°C per minute to 250°C where the temperature was held. Carrier gas was helium at a flow of 6 cm^3/min. There was no split on the sample injected into the column and a FID detector was used. Initial fractionation of the samples was carried out by vacuum distillation.

RESULTS AND DISCUSSION

Reduction in ash levels

In the first series of experiments toluene was used as the solvent and the extractions were carried out at a temperature of 110°C. The ratio of extract to toluene was varied and a blank run was also carried out with no toluene added. This was to make certain that no precipitation was occurring as a result of cooling and reheating the filtered extract solution. These results are shown in Table 2,

From the results in Table 2 it can be seen that by increasing the quantity of toluene used then the amount of material precipitated is increased and the ash level of the filtrate decreases. It is clear, from the filtrate mass, that there is still a significant quantity of toluene remaining. At the temperature used this might be expected. To allow for this an equivalent extract ash is calculated as shown in Table 2. This figure also shows a steady decrease as the mass of toluene used increases. The mass of cake obtained shows that there would be a significant loss of product, by precipitation, if this method were to be used to remove trace elements. The extract solution used in this series of experiments had a "high" ash value of 0.056%. In the next set of experiments an extract solution with a lower ash value of 0.018% was used and the effect of varying the extract temperature was studied.

Table 3 shows that as the temperature of extraction is increased, then the mass of cake decreases, but the equivalent extract ash increases. However, it would seem that a significant reduction in the amount of material precipitated can be obtained without a large

856

increase in the ash level of the filtrate. This is especially seen
in the increase in temperature from 100 to 138°C.

All the above experiments were carried out by mixing the extract
and toluene together cold in the autoclave and then heating to the
extraction temperature. In a commercial operation, the solvent
would probably be added to a hot extract. This was simulated by
injecting toluene into heated extract at the required temperature.
The results obtained were similar to those shown in Tables 2 and 3.

Table 4 shows the results obtained when THF is used as the solvent.
The reason THF was tried was that the normal value of the THF
insolubles is about 2-4%, but it was noted [18] that over 60% of the
trace elements precipitated out with the insolubles. Thus, it may
be possible to reduce the trace element concentration with only a
small amount of material precipitated. However, the results
obtained from these experiments show that THF gave little, if any,
reduction in ash level in the extract solution.

The results for toluene show that it is possible to reduce the
trace element concentration in filtered extract solutions using
this method. There is a price to pay, however, and that is loss of
product as precipitated material. This can be reduced by increasing
the extraction temperature to an optimum level. However, the value
of this lost product is questionable, since it will be mainly
preasphaltenic, difficult to convert to useful products in the
hydrocracking stage and could be responsible for much of the carbon
deposition on the hydrocracking catalyst.

Trace element concentrations

Not only is the overall ash level important in the coal extract
solution, which is fed to the hydrocracking stage, but also the
concentration of the individual trace elements. Table 5 shows the
concentration of trace elements in the ash from the original
extract and the filtrate produced after toluene extraction. This
was for an extract with an ash level of 0.035%, extracted with
toluene at 165°C to give a filtrate with an ash level of 0.01%. The
results show that there are some differences, with calcium reducing
and iron and titanium increasing their proportions. However, the
changes are not great and it would be expected that if the filtrate
were fed to the hydrocracker it would deposit trace elements as
observed previously [2], except, of course, there would be a smaller
quantity overall.

Nature of the extract solution after precipitation

When toluene extractions were carried out at 110°C it was clear
that toluene remained in the filtrate from the mass obtained. With
the higher temperature extractions the filtration was also carried
out at the same temperature and the mass of filtrate was
accordingly lower as most of the toluene was boiled off from the
filtrate. However, examination of the filtrate showed that it was
much more fluid than the original extract and it appeared that some
toluene remained in it. Analysis of the extract and filtrate were

carried out using an initial vacuum distillation and GC analysis as described previously. The aim being to find how much toluene remained. However, no toluene was seen in the chromatogram.

Table 6 shows some results obtained for the simulated distillation of extract and filtrate after toluene extraction. It can be seen that the fraction boiling up to 150°C is reduced after extraction, contrary to expectations, and that the fraction from 200-300°C increases, mainly in the 250-300°C range. Examination of the chromatogram shows no difference in the actual components present, only differences in their quantity. With the low boiling material the reduction is probably a consequence of the heating at elevated temperatures during filtration coupled with the stripping of the toluene. The reason for the increase in the other ranges is not known and more extensive analysis is required to answer this problem.

ACKNOWLEDGEMENTS

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Table 1 Analysis of Point of Ayr Coal

Proximate analysis			Elementary Analysis				
VM	Ash	Moisture	C	H	N	O	S
(wt% db)		%			(wt% dmmf)		
31.6	13.1	3.5	82.7	5.2	1.8	7.5	2.8

Table 2 Extraction of coal extract solution with toluene
       — effect of toluene to extract ratio

Temperature of extraction : 110°C
Ash of original coal extract solution : 0.056%

Mass Extract	(g)	56	55	61.3	55	55
Mass Toluene	(g)	56	32	24.5	11	0
Ratio Extract/Tol		1:1	1.7:1	2.5:1	5:1	BLANK
Filtrate – Mass	(g)	81.3	66.1	79.0	62.3	
– Ash	(%)	0.007	0.014	0.038	0.047	0.055
Cake – Mass	(g)	18.7	15.4	3.0	1.5	
– Ash	(%)	0.255	0.185	0.19	0.285	NO
Equivalent						EFFECT
Extract Ash	(%)	0.011	0.016	0.049	0.053	

Note: Equivalent Extract Ash = $\dfrac{\text{Mass Filtrate} * \text{Filtrate Ash}}{\text{Mass Extract}}$

Table 3 Extraction of coal extract solution with toluene
       — effect of temperature

Ratio extract/toluene : 1.67:1
Ash of original coal extract solution : 0.018%

Extraction Temp	(°C)	100	138	175	200
Mass Extract	(g)	50	50	46.5	50
Filtrate – Mass	(g)	51.6	59.1	55.7	50.1
Ash	(%)	0.006	0.007	0.008	0.014
Cake – Mass	(g)	20.4	10.0	6.9	3.4
Ash	(%)	0.205	0.16	0.44	2.2
Equivalent					
Extract Ash	(%)	0.006	0.007	0.01	0.014

Table 4 Extraction of coal extract solution with THF

Ash of original coal extract solution : 0.018%

Extraction Temp	(°C)	122	103	66	66
Mass Extract	(g)	50	50	50	50
Mass THF	(g)	30	30	30	50
Ratio Extract/THF		1.67:1	1.67:1	1.67:1	1:1
Filtrate – Mass	(g)	55.1	59.3	69.6	81.5
– Ash	(%)	0.012	0.013	0.016	0.011
Cake – Mass	(g)	4.1	4.8	4.8	9.5
Equivalent					
Extract Ash	(%)	0.013	0.015	0.022	0.018

Table 5 Trace element analysis

	Original Extract	Filtrate after Toluene extraction
Proportion of Element in Ash (%)		
Al	5.5	6.3
Ti	1.8	4.0
Si	4.0	2.8
Ca	25.6	15.2
Mn	3.0	4.5
Fe	3.8	8.2
Mg	5.4	5.4
Na	1.5	2.4
K	0.5	0

Table 6 Simulated distillation of extract and filtrate after extraction with toluene at 165°C

	Original Extract	Filtrate 1	Filtrate 2	3
		(%)		
0-100°C	0.47	0.05	0.04	0.06
0-150°C	1.21	0.10	0.08	0.09
0-200°C	6.97	5.11	4.28	4.18
0-250°C	19.3	32.9	20.0	21.1
0-300°C	54.6	78.5	64.1	67.5
0-350°C	100	100	100	100

Extracts prepared with an extract:toluene ratio of:
1: 1.6/1
2: 2.5/1
3: 3.3/1

Fig.1. A comparison of the plastometry curves for coal H1 at 0.5 and 5 MPa (Heating Rate 3 °C min^{-1})

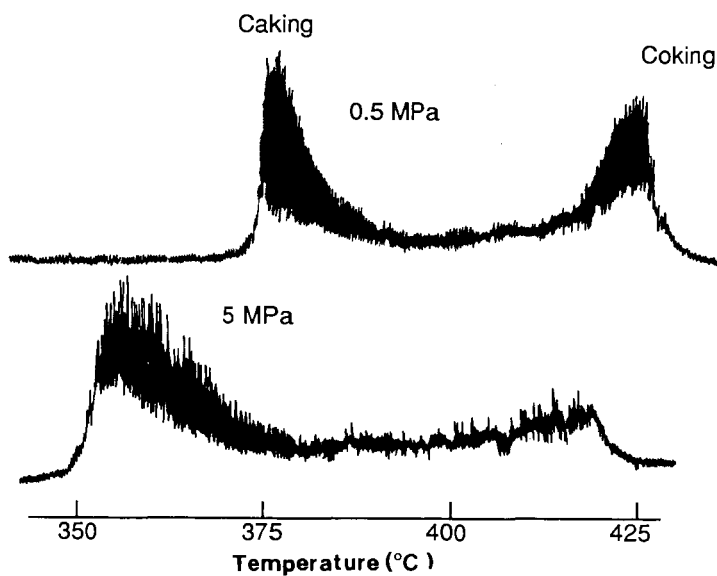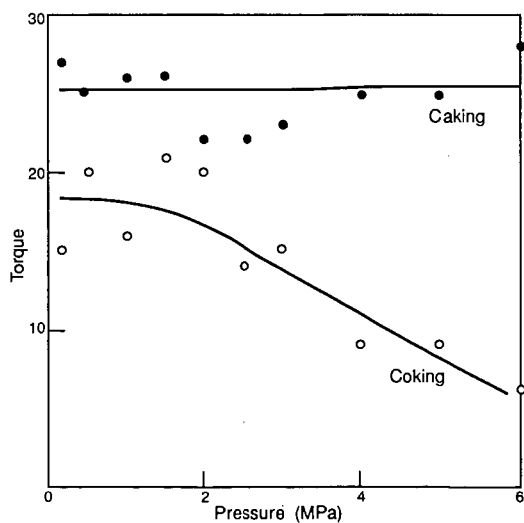**Fig. 1. A comparison of the plastometry curves for coal HI at 0·5 and 5MPa(heating rate 3°Cmin^{-1})**

Fig.2. The variation of plastometry torque parameters with
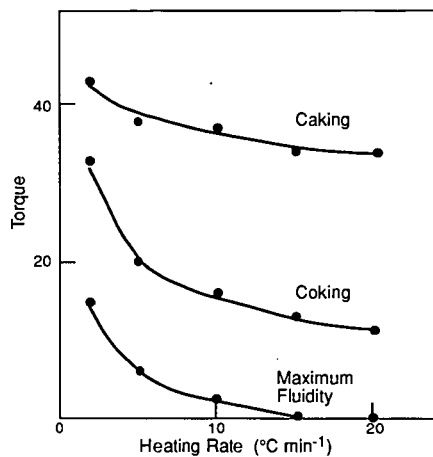pressure for Coal H1 (Heating Rate 3°C min⁻¹)

Fig.3. The variation of plastometry torque parameters with heating rate for coal H1 (Pressure 2 MPa)
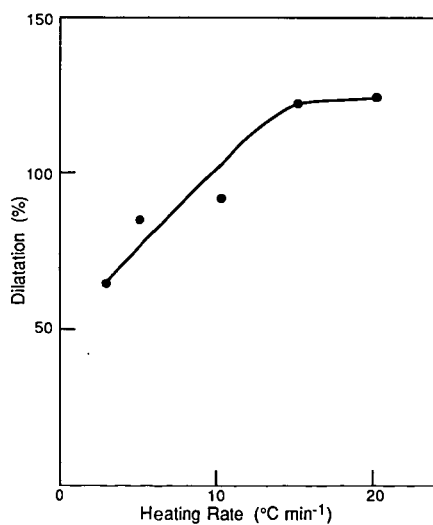

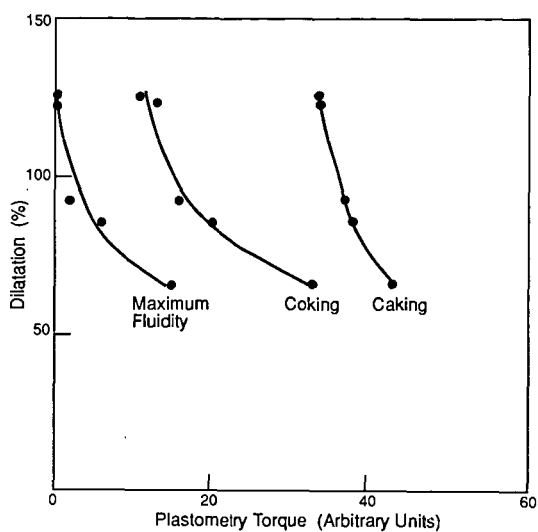Fig.4. The effect of heating rate on the dilatation of coal Oa (Gauge pressure - 2 MPa)

Fig.5. The variation of dilatation with plastometry torque
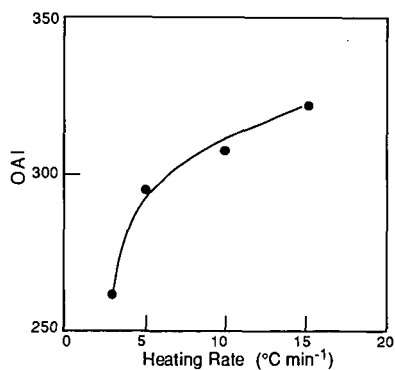parameters at 2 MPa pressure for coal Oa

Fig.6. The variation of optical anisotropy index (OAI)
with heating rate for coal Oa (Pressure 2 MPa)

865

ACTIVITY AND CHARACTERIZATION OF COPROCESSING CATALYSTS PRODUCED FROM AN IRON PENTACARBONYL PRECURSOR

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ABSTRACT

It is generally believed that highly dispersed catalysts are very effective in the conversion of coal to liquids, but the effects of dispersion and composition have not been adequately investigated. We chose to study the use of iron pentacarbonyl, $Fe(CO)_5$, to produce a highly dispersed catalyst *in situ* in the coprocessing of Illinois #6 coal and Maya ATB residuum. The activity of the catalyst produced from this precursor has been investigated, and its particle size and composition measured using X-ray diffraction, Mössbauer spectroscopy, and transmission electron microscopy (TEM). Use of 0.5 wt% Fe added as $Fe(CO)_5$ resulted in an increase in coal conversion to methylene chloride solubles from 39% to 82%. The $Fe(CO)_5$ precursor decomposed in the reactor to produce a mixture of highly dispersed pyrrhotite, $(Fe_{1-x}S)$, Fe_3C, and other iron compounds. However, with time at reaction conditions, 95% of the iron was converted to $Fe_{1-x}S$. The pyrrhotite particles formed in the initial stages of reaction had a mean crystallite size of 12 nm when measured using X-ray diffraction line broadening; the small particle sizes were confirmed by TEM and Mössbauer studies.

INTRODUCTION

Coprocessing is the liquefaction of coal in a heavy petroleum medium such as a heavy crude or residuum. Conventional direct liquefaction processes must recycle two-thirds of the coal-derived oil, but coprocessing can operate completely or largely in a "once through" mode, eliminating the cost and complication of the large recycle. (1) In addition, metallic impurities in the oil deposit on the coal residue or pitch.

In most direct coal liquefaction processes, the use of catalysts results in more desirable products under less severe processing conditions. The same is true for coprocessing, which may require even more effective catalysts because the petroleum-derived slurrying oils used in coprocessing are often poor hydrogen donors. In direct coal liquefaction, supported metal catalysts (e.g. $CoMo/Al_2O_3$) may suffer from poor contact between the coal and the catalyst. Unsupported dispersed catalysts can offer good contact between the coal and the catalyst. As early as 1924 it was known that the addition of iron sulfides to the liquefaction mixture would improve yields. (2) Addition of low surface area solids requires high catalyst concentrations. Particulate pyrite addition has been studied and found effective in concentrations of 10wt%. (3)

One method of increasing dispersion (surface area per mass) is to introduce the catalyst as a soluble precursor. Such precursors are distributed throughout the coal-oil mixture by

dissolving in the oil, and they decompose upon heating or other treatment to form very small catalyst particles within the coal-oil mixture. The high dispersion allows catalyst concentrations of less than 1.0wt% to be used. Examples of these catalyst precursors are nickel acetate, (4) carboxylic salts of iron or molybdenum, (5) water-soluble ammonium molybdate, (6) molybdenum naphthenate (7), and carbonyl compounds of iron, molybdenum, and other metals. (8) Crystallite sizes as low as 15-30nm have been reported for a Ni acetate precursor. (4)

Several studies have reported the use of $Fe(CO)_5$ and other iron carbonyls in direct liquefaction in a hydrogen-donating solvent.(9-12) These studies showed that the $Fe(CO)_5$ precursor produced a catalyst active for hydroliquefaction of coal using Fe at 2.0wt% of the feed coal. The precursor was converted to a less active iron oxide (Fe_3O_4) in the absence of added sulfur, but when sulfur was added in the form of elemental sulfur or organic sulfur compounds, the more active iron pyrrhotite ($Fe_{1-x}S$) was formed. (10) Increases in coal conversion were found with both bituminous and subbituminous coals. (11) The use of other soluble precursors such as cyclopentadienyliron dicarbonyl dimer, $(C_5H_5)_2Fe_2(CO)_4$, yielded increased coal conversions of the same order of magnitude as $Fe(CO)_5$. (8) However, particle sizes of liquefaction catalysts produced from the decomposition of $Fe(CO)_5$ have not been reported in the literature, but other studies have shown that iron particles less than 10nm in diameter can be deposited on carbon or zeolite supports by thermal decomposition. (12,13)

EXPERIMENTAL

Illinois #6 (Burning Star) hvB bituminous coal ground to -200 mesh ($<74\mu m$) was obtained from the Pittsburgh Energy Technology Center and used as received. Maya ATB (650°F+) residuum was obtained from Citgo. Analysis of the coal is shown in Table 1. The Maya ATB had a composition of 85.9%C, 10.2%H, 0.5%N, and 4.8%S, with a Conradson Carbon residue of 15.2%. Iron pentacarbonyl was obtained from Strem Chemical and filtered through glass wool when necessary to remove iron particles produced by decomposition of the carbonyl.

Table 1. Ultimate and Proximate Analyses of Illinois #6 Coal

	wt.%		wt.%
Carbon	74.0	Organic Sulfur	0.96
Hydrogen	5.65	Moisture	3.80
Nitrogen	1.58	Volatile Matter	40.5
Sulfur	3.07	Fixed Carbon (diff.)	48.7
Ash	10.8		
Oxygen (diff.)	4.90		

Ultimate analysis is on a dry basis
Analyses performed by BCR National Laboratory

Coprocessing experiments were conducted in a 300ml stainless steel autoclave (Autoclave Engineers) agitated by a turbine impeller and heated by a tube furnace. Coal (12.5g, as rec.), 37.5g Maya ATB residuum, and from 0-8.8g (0-5wt%Fe) catalyst precursor were placed into the reactor, which was flushed with helium and stirred at 50°C for two hours

to ensure mixing of the precursor in the viscous residuum. The reactor was pressurized with hydrogen to 6.9 MPa, heated to 425°C in approximately 40 minutes, and held at 425°C for 60 minutes while stirring at 1300 rpm. The reactor was then cooled to below 300°C in about five minutes. Conversion was determined using Soxhlet extraction with methylene chloride. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles were determined by adding 40 volumes of n-pentane to the methylene chloride (CH_2Cl_2) solubles, and using Soxhlet extraction with pentane.

A Phillips X-ray Diffractometer using Cu-Kα radiation at 30kV and 20mA was used to obtain powder diffraction patterns of the catalysts. The Scherrer equation was used to calculate average crystallite sizes from line broadening of the peaks, corrected for instrumental broadening. (14) Mössbauer spectroscopy was performed using a 100 mCi source at both room temperature (290K) and cryogenic temperatures (10K, 80K). Transmission electron microscopy was carried out using a JEOL 2000FX STEM (100kV beam) with an energy dispersive X-ray spectrometer. A Bruker MSL 300 FT-nuclear magnetic resonance spectrometer was used to obtain the carbon aromaticity (f_a) of soluble coprocessing products.

RESULTS AND DISCUSSION

Coprocessing of Illinois #6 coal with Maya ATB was carried out with varying amounts of $Fe(CO)_5$ precursor. The conversion to methylene chloride solubles increased rapidly as the catalyst concentration was raised from 0 to 0.5 wt% Fe (based on the total coal + residuum feed), but increased much more slowly from 0.5 to 5wt% Fe (Figure 1). The use of only 0.2 wt% Fe was sufficient to increase conversion to 65%, vs. 39% for the no-catalyst case. The fact that an amount of iron considerably less than that already present in the coal can produce such an increase shows the benefit of using a precursor which will give high dispersion.

The effect of the iron catalyst produced from the precursor appears to be limited to conversion of the coal rather than hydrogenation of the residuum or subsequent upgrading of the coal liquids produced. Catalyst addition produced little change in the asphaltene fraction of the product (it increased from 12% of the product to 15%). Table 2 shows that the H/C ratio of the products does not change significantly with catalyst addition, and heteroatoms are not removed to any appreciable extent. The aromaticity (f_a) of the CH_2Cl_2 solubles does increase with catalyst addition due to the high aromaticity of the additional liquids produced from the coal.

Table 2. Analyses of CH_2Cl_2 Solubles from Coprocessing using a $Fe(CO)_5$ Catalyst Precursor

$Fe(CO)_5$ (wt% Fe)	C	H	N	S	H/C(atom)	f_a
	wt.%, as received					
0.0	83.3	10.5	0.2	2.6	1.49	0.36*
2.5	83.1	10.6	n.d.	2.6	1.53	0.40
5.0	84.0	10.6	0.3	2.4	1.51	---

*f_a of Maya ATB is 0.33

XRD and Mössbauer spectroscopy were used to determine the composition and

dispersion of the catalysts produced from $Fe(CO)_5$. The results are presented in Table 3. The properties of the catalyst at various stages of reaction were of interest, so a number of samples of insoluble coprocessing residue were analyzed. The first sample (referred to as 425°C - 0 min.) was prepared by heating a mixture of coal, residuum, and $Fe(CO)_5$ (2.5 wt% Fe) to the reaction temperature of 425°C, then cooling the mixture immediately. This sample represents the condition of the catalyst before extensive coal conversion has taken place. X-ray diffraction patterns of this sample showed a fully developed pyrrhotite pattern. This result agrees with the results of Suzuki et al. (10), and should be expected since the Maya residuum is high in sulfur (4.84 wt%). A line broadening calculation on the largest pyrrhotite peak gave an average crystallite diameter of 12.0nm.

The second sample (425°C - 60 min.) consisted of the insoluble residue which remained after reaction of coal, residuum, and $Fe(CO)_5$ for 60 minutes at 425°C. This sample represented the state of the catalyst after it had spent a longer time under the reaction conditions. This sample also showed a pyrrhotite pattern, but with an average crystallite diameter of 20.5nm. The increase in crystallite size is likely due to the sintering of small metal catalyst particles which commonly occurs at elevated temperatures. (15) Djega-Mariadassou et al. found that when iron oxide aerosols (<80nm) were used as liquefaction catalysts, the small particles were very sensitive to sintering, but in the presence of coal the effect was inhibited. (16) This was attributed to the coal depositing heavy organic residues on the surface of the catalyst.

In order to distinguish the iron added as $Fe(CO)_5$ from the iron originally present in the coal, XRD and Mössbauer spectroscopy were performed on a sample of Illinois #6 coal and on a coprocessing residue to which no catalyst had been added. Table 3 shows that the coal exhibited only a weak diffraction pattern for FeS_2, and that the coprocessing sample without added $Fe(CO)_5$ gave a weak $Fe_{1-x}S$ pattern. Since these patterns were weak compared to the samples with added catalyst, it was concluded that the XRD signal was mostly due to the added catalyst.

Mössbauer spectroscopy confirmed the presence of the pyrrhotite detected by XRD, but revealed some other species which were, perhaps because of their small particle size or lack of crystallinity, invisible to XRD. The 425°C - 0min. sample was found to consist of only 26% pyrrhotite, with about an equal amount of iron carbide and almost 50% of iron oxide/oxyhydroxide. The oxide/oxyhydroxide may have been produced in the reaction, or it may have been originally α-Fe which was oxidized when the sample was exposed to air. In any case, it is interesting to see that the precursor may form a variety of iron compounds in the reactor. The source of the iron carbide is probably $Fe(CO)_5$ and not the pyrite originally in the coal, since the transformation of pyrite to iron carbide is thermodynamically unfavorable under these conditions. Cook and Cashion have also observed the formation of iron carbide from $Fe_3(CO)_{12}$ when they used it as a catalyst precursor in the liquefaction of a brown coal. (17) Mössbauer analysis of the 425°C - 60 min. sample showed that after 60 minutes at the reaction conditions, most of these intermediates had been transformed to pyrrhotite, with a small amount of iron oxide remaining. In the high-sulfur environment of the coprocessing reaction, it is thermodynamically favorable for all of the iron to be converted to pyrrhotite.

The Mössbauer results show that the pyrrhotite was not the common mineralogical type, monoclinic Fe_7S_8, but was a somewhat poorly formed intermediate variety. In addition to the composition, the Mössbauer spectra provided information as to the size of the catalyst particles. There was a significant difference between the room temperature spectrum and those obtained at cryogenic temperatures, indicating the presence of superparamagnetic iron-bearing particles, which only occurs when particles are on the order of 20nm or less. (18)

Transmission electron microscopy was employed to independently verify the size range of the iron-containing particles produced from the $Fe(CO)_5$ precursor. To eliminate interference of the iron and other mineral matter in the coal, a model catalyst system was used which consisted of activated carbon with iron deposited on it. The model catalyst was produced by heating a mixture of activated carbon (with a very low iron content), toluene

Table 3. X-ray Diffraction and ^{57}Fe-Mössbauer Data for
Products of Fe(CO)$_5$ Decomposition

| Sample	^{57}Fe Mössbauer Phases (%iron)	XRD - Iron Phases Identified (mean diam.)
Coprocessing Residue 425°C, 0 min. Fe(CO)$_5$ precursor	Fe$_{1-x}$S (26%) Fe$_3$C (25%) Iron oxide/FeOOH (49%)	Fe$_{1-x}$S (12.0nm)
Coprocessing Residue 425°C, 60 min. Fe(CO)$_5$ precursor	Fe$_{1-x}$S (95%) Iron oxide (5%)	Fe$_{1-x}$S (20.5nm)
Coprocessing Residue 425°C, 1hr. No catalyst added	Fe$_{1-x}$S (~100%) Iron oxide (trace)	Fe$_{1-x}$S - trace
Illinois #6 coal - Before Reaction	Pyrite (87%) FeSO$_4$:H$_2$O (8%) Ferric sulfate (5%) FeOOH (trace)	FeS$_2$ - trace

(solvent), and Fe(CO)$_5$ in an autoclave to decompose the precursor into small particles, some of which would end up on the carbon support. The TEM/STEM images of this catalyst system revealed a wide distribution of particle sizes, with many particles between 10-100nm. Energy dispersive analysis of the X-rays emitted from the sample confirmed that the small particles which were observed contained iron, while the matrix as well as the activated carbon blank contained no detectable iron. A typical micrograph is shown in Figure 2, exhibiting the iron-bearing particles (small, dark spots) on the more transparent background of the larger activated carbon particle.

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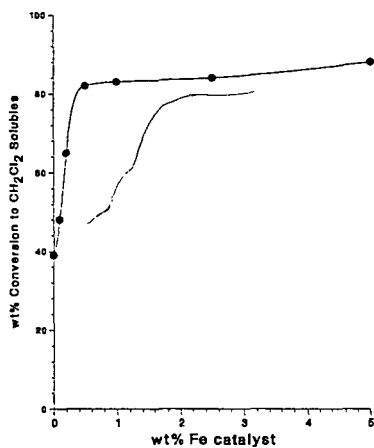
Figure 1. Coal Conversion vs. Amount of Fe(CO)$_5$ Precursor
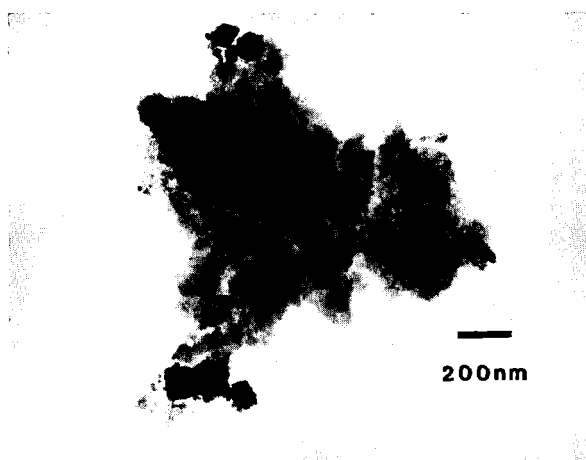
Figure 2. TEM/STEM Micrograph of Iron-Containing Particles Deposited on Activated Carbon by Thermal Decomposition of Fe(CO)$_5$

THE EFFECT OF MILD ALKYLATION PRETREATMENT ON
LIQUEFACTION REACTIVITY OF ARGONNE COALS

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INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to
develop methods for dissolving coal at low reaction severity (perhaps
defined as temperatures below 350 °C and pressures of 1000-1500 psig).
Researchers at the Pittsburgh Energy Technology Center (1), the North
Dakota Energy Research Center (2), Carbon Resources, Inc. (3), and the
Colorado School of Mines (4) have investigated various methods for
improving coal reactivity and liquid yields at mild reaction
conditions. These studies showed that coal can be readily converted
to THF soluble products via selective chemical attack rather than
thermal bond scission, but that the rate and extent of coal
dissolution at mild conditions is strongly dependent upon intrinsic
coal reactivity. Thus the problem of optimizing low severity
liquefaction performance becomes one of maximizing coal reactivity at
these conditions.

The objective of this paper is to describe our efforts to improve
intrinsic coal reactivity using mild acid-catalyzed alkylation as a
pretreatment prior to liquefaction. The basis for this work derives
from studies by Sternberg (5), Larsen (6), Sharma (7), and others
where alkylation was utilized as a method for rendering coal soluble
in THF or toluene to aid in structural analysis. Results from
Sharma's work are particularly pertinent, since they demonstrate the
ability to alkylate coal using alkyl alcohols rather than exotic and
expensive chemical reagents such as tetrabutylammonium hydroxide,
aluminum trichloride, methyl iodide, etc. Limited work has been
reported which relates increased solvent solubility of alkylated coal
to enhanced liquefaction reactivity. Schlosberg et al. (8) measured
the reactivity of mildly alkylated Wyodak subbituminous and Illinois
#6 bituminous coals in tetralin at 427 °C, 1500 psig hydrogen pressure
and 130 minutes reaction time. A 10-21 wt% (MAF and alkyl group-free
basis) increase in cyclohexane soluble conversion was noted for the
alkylated coals.

EXPERIMENTAL PROCEDURE

Pocahontas low volatile bituminous coal, Illinois 6 high volatile
bituminous coal, Wyodak subbituminous coal, and Beulah-Zap lignite
from the Argonne Premium Sample Bank were used as feed coals in these
experiments. Ultimate analyzes for these coals are listed in Table I.

Table II summarizes the alkylation reaction conditions studied. Each
experiment was performed at ambient conditions by suspending 5 g of
coal in 40 cm^3 of alkyl alcohol and 0.1 cm^3 of concentrated H_2SO_4
catalyst. After the prescribed reaction time, remaining alcohol was
removed by roto-evaporation followed by vacuum drying (50 °C, 24
hrs.). Untreated coal samples were vacuum dried at the same
conditions before liquefaction. Carbon analyses were performed on
each alkylated coal sample using a Carlo-Erba model 1106 CHN analyzer

873

to measure the extent of alkylation as computed from the following
formula:

$$\text{Extent of alkylation} \atop \text{(g alkyl group/100 g MAF coal)} = \frac{C_3 - C_1}{C_2 - C_3} \times 100$$

where: C_1 = wt% carbon (MAF basis) in untreated coal
C_2 = wt% carbon in alkyl group
C_3 = wt% carbon (MAF basis) in alkylated coal

Liquefaction reactivity experiments were conducted in a 20 cm^3 tubing
bomb reactor attached to an agitator and immersed in a fluidized
sandbath. Table III lists reaction conditions used in these runs. A
non-hydrogen donor vehicle (1-methylnaphthalene) and a hydrogen donor
vehicle (9,10-dihydrophenanthranene) were used as solvents (2/1
solvent/coal ratio). Coal conversion was monitored using
tetrahydrofuran (THF) extraction data corrected for the intrinsic THF
solubility of untreated and alkylated coals.

Solubility measurements were conducted at ambient conditions and
consisted of: 1) sonicating the liquid products from the tubing bomb
reactor in excess THF, 2) centrifuging the mixture, and 3) decanting
THF-soluble products and excess THF from the THF-insoluble residuum.
This procedure was repeated at least two times or until no additional
THF-insoluble products were recovered. The THF insolubles were
vacuum-dried (100 $^{\circ}$C, 24 hrs) to remove residual THF, weighed, and
finally ashed. Coal conversion to THF soluble products was computed
as follows:

$$\text{Coal conversion} \atop \text{(wt% MAF basis)} = \frac{M_f - M_p}{M_f} \times 100$$

where: M_f = mass of MAF THF-insoluble coal charged

M_p = mass of MAF THF-insoluble products recovered
(corrected to satisfy the ash balance)

Photoacoustic Fourier Transform Infrared Spectroscopy (PAFTIR) was
used to monitor functional group changes within the coal resulting
from alkylation. The photoacoustic technique allows direct
measurement of powdered solid state spectra without errors caused by
low transmittance signals or variations in surface morphology. PAFTIR
spectra generally measure solid properties to depths of about 40
angstroms.

RESULTS AND DISCUSSION

Alkylation Studies
Experiments were completed to study the effects of coal rank, alkyl
group size, reaction time, and acid catalyst concentration on the
extent of coal alkylation. Results from several of these runs are
shown in Table IV. As mentioned earlier, all pretreatment studies
were conducted at ambient temperature and pressure. The extent of
alkylation increased with decreasing coal rank and roughly in
proportion to each coal's oxygen content. As discussed later, this
observation can be attributed to 0-alkylation at phenolic and
carboxylic sites in the coal. The extent of alkylation for Wyodak
coal was less than 1.0 alkyl groups/100 carbon atoms using methanol or
ethanol, but increased dramatically with n-propanol, n-butanol, or
isobutanol. Other experiments using higher alcohols suggested that no

significant improvement in the extent of alkylation would be achieved over that obtained with n-propanol.

Approximately 50% of the ultimate extent of Wyodak coal alkylation was achieved in 30 minutes time, suggesting that highly reactive phenolic and carboxylic sites in the coal can be alkylated very quickly. The extent of alkylation increased with increased acid concentration below about 1.0 vol%. Higher acid concentrations had little effect on the extent of alkylation. Thus, it appears possible to mildly alkylate coal by varying the alkyl alcohol, reaction time, and acid contentration used.

Liquefaction Reactivity Studies
To study the effect of mild alkylation on liquefaction reactivity, samples of the four Argonne coals propylated for 3 hours with 1.0 vol% sulfuric acid catalyst were liquified in 1-methylnaphthalene solvent at low severity reaction conditions. Conversion results for these runs are summarized in Figure 1. Data for the corresponding untreated Argonne coals are included in this figure for ease of comparison. Propylation of each coal enhanced conversion to THF soluble products, although the effect increased dramatically with decreasing coal rank. A rough correlation was noted between the extent of propylation and improvement in liquefaction reactivity.

Figure 2 shows results from a series of low severity experiments using Wyodak coal which was alkylated with methanol, ethanol, n-propanol, n-butanol, and isobutanol (3 hrs, 1.0 vol% acid). These data suggest only a slight effect of alkyl group chain length on reactivity enhancement indicating that cheaper, commodity alcohols such as methanol may be used successfully as alkylating agent. This result indicates the potential for considering mild alkylation pretreatment on a larger process scale, although net methanol consumption must be better estimated before costs associated with alkylation pretreatment can be determined.

Finally, Figure 3 shows the effect of reaction temperature on the liquefaction reactivity of methylated (3 hrs, 1.0 vol% acid) and untreated Wyodak coals using DHP solvent. Clearly, mild alkylation pretreatment enhances reactivity over a range of conversion levels. This result is significant since it shows that mild alkylation may be a beneficial pretreatment even at conversion levels of commercial interest.

PAFTIR Studies
In an attempt to begin studying the reaction mechanisms governing our mild alkylation process, we analyzed each untreated and alkylated coal using Photoacoustic Fourier Transform Infrared Spectroscopy. Figure 4 shows the subtractive spectrum (alkylated coal spectrum minus untreated coal spectrum) for propylated Wyodak coal (3 hrs, 1.0 vol% acid). Several important features of this spectrum can be identified: 1) reduced O-H stretching in the 3200-3600 cm^{-1} region, 2) increased aliphatic C-H stretching between 2800 and 3000 cm^{-1}, 3) appearance of the C=O ester stretch near 1700 cm^{-1}, 4) disappearance of the C=O carboxylate stretch near 1550 cm^{-1}, and 5) appearance of C-O aliphatic and aromatic stretchs near 1000 cm^{-1}.

These observations are consistent with the dehydration and esterification reactions shown in Figure 5. Both reactions act to reduce hydrogen bonding within the coal structure which may have a direct positive impact on liquefaction reactivity. More indirectly,

these reactions lower the concentration of OH species in coal-derived products and hence, reduce the extent of retrogressive condensation via ether bridge formation. Reducing production of THF-insoluble condensation products increases the net THF-soluble coal conversion measured during the liquefaction experiment. What is unknown at this point is why such a small extent of reaction (perhaps less than 20% of the OH groups are typically alkylated) results in significant reactivity enhancement. None of the spectra collected have shown any significant evidence of C-alkylation.

SUMMARY AND CONCLUSIONS

Acid-catalyzed alkylation pretreatment of four Argonne coals using alkyl alcohols has been investigated as a method for improving liquefaction reactivity. The extent of alkylation increased with decreasing coal rank and, to some extent, increasing alkyl group size. Infrared spectroscopic studies of the treated and untreated coals indicated that alkylation occurred at phenolic and carboxylic sites within the coal, but no evidence of C-alkylation was noted. Mild alkylation pretreatment improved liquefaction reactivity for each coal studied over a range of reaction severity. The improvement in liquefaction reactivity correlated roughly with the extent of alkylation achieved.

ACKNOWLEDGEMENT

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Table I

ULTIMATE ANALYSIS OF FEED COALS

Wt% Dry Basis	Illinois #6	Pocahontas #3	Wyodak	Beulah-Zap
Carbon	65.7	86.7	68.4	65.9
Hydrogen	4.2	4.2	4.9	4.4
Nitrogen	1.2	1.3	1.0	1.0
Sulfur	4.8	0.7	0.6	0.8
Oxygen	8.6	2.3	16.3	18.2
Ash	15.5	4.8	8.8	9.7
Coal Rank	HVB	LVB	Subbit.	Lignite

Table II

ALKYLATION REACTION CONDITIONS STUDIED

Temperature: ambient (approx. 25 ^{o}C)

Pressure: ambient (approx. 0.85 atm)

Reaction Time: 0.5 - 24 hours

Alkylating Agent: methanol, ethanol, n-propanol, n-butanol, isobutanol

Catalyst: sulfuric acid (0.1 - 3.0 vol%)

Table III

LIQUEFACTION REACTION CONDITIONS STUDIED

Temperature: 315 ^{o}C, 350°C, 400°C

Pressure: 65 atm (initial, cold)

Reaction Time: 30 minutes

Feed gas: hydrogen

Solvents: 1-methylnaphthalene, 9,10-dihydrophenanthrene

Solvent/Coal weight ratio: 2/1

Table IV

RESULTS OF AMBIENT ALKYLATION PRETREATMENT EXPERIMENTS

Coal*	Alcohol	Time (hrs.)	Acid Conc. (vol%)	Extent of Alkylation (groups/100 C atoms)
Ill.	n-propanol	3.0	1.0	1.2
Poc.	n-propanol	3.0	1.0	0.7
Wyo.	n-propanol	3.0	1.0	3.8
B-Z.	n-propanol	3.0	1.0	2.7
Wyo.	methanol	3.0	1.0	0.7
Wyo.	ethanol	3.0	1.0	0.6
Wyo.	n-butanol	3.0	1.0	3.9
Wyo.	isobutanol	3.0	1.0	3.7
Wyo.	n-propanol	0.5	1.0	2.5
Wyo.	n-propanol	1.0	1.0	2.9
Wyo.	n-propanol	6.0	1.0	4.3
Wyo.	n-propanol	24.0	1.0	4.6
Wyo.	n-propanol	3.0	0.1	0.6
Wyo.	n-propanol	3.0	0.5	1.0
Wyo.	n-propanol	3.0	2.0	3.6
Wyo.	n-propanol	3.0	3.0	4.0

* Ill. = Illinois #6   Wyo. = Wyodak
   Poc. = Pocahontas #3   B-Z = Beulah-Zap
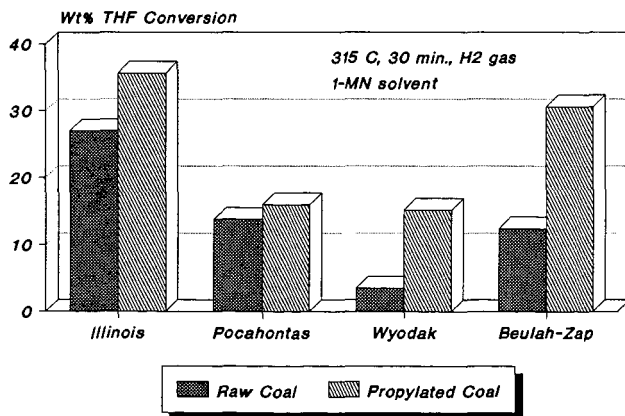
Figure 1. Effect of Propylation on Argonne Coal Liquefaction
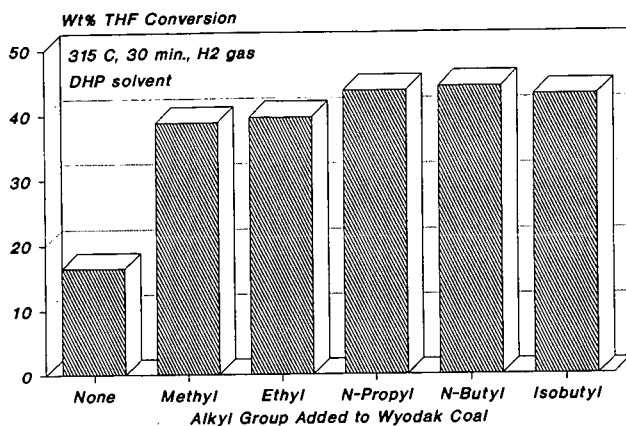   Reactivity at Low Severity Conditions

Wt% THF Conversion

315 C, 30 min., H2 gas
DHP solvent

Alkyl Group Added to Wyodak Coal

Figure 2. Effect of Alkyl Group Addition on Low Severity Wyodak
Coal Liquefaction Reactivity

Wt% THF Conversion

Wyodak Coal, 30 min., H2 gas, DHP solvent

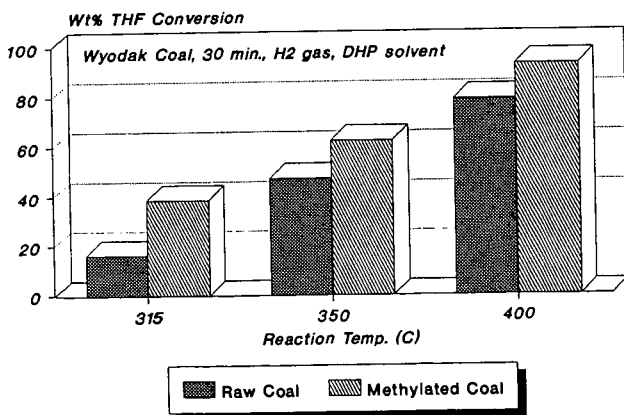Reaction Temp. (C)

Raw Coal   Methylated Coal

Figure 3. Effect of Reaction Temperature on Liquefaction
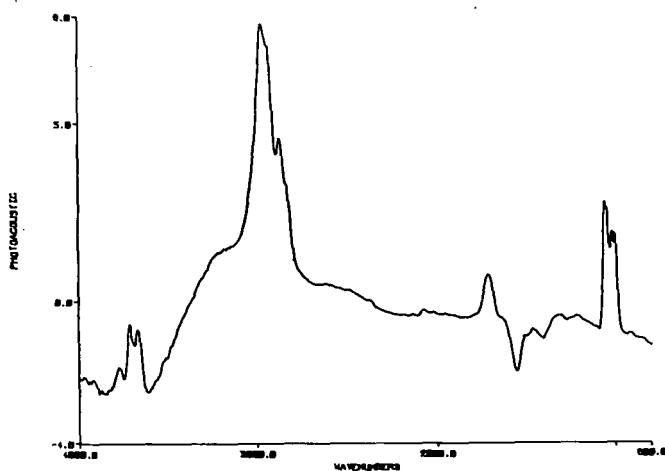Reactivity of Methylated and Untreated Wyodak Coal

Figure 4. Subtractive Spectrum of Propylated Wyodak Coal
Collected Using Photoacoustic Fourier Transform
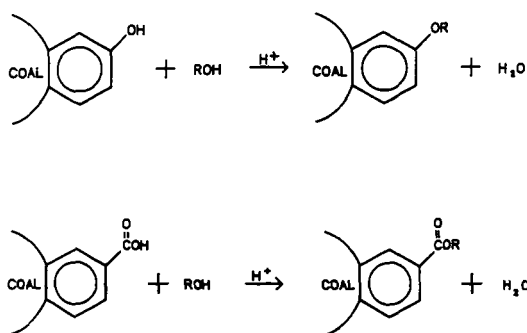Infrared Spectroscopy

Figure 5. Phenolic Dehydration and Carboxylic Acid
Esterification Reactions Occurring During Mild
Alkylation Pretreatment

USE OF DISPERSED CATALYSTS FOR COAL LIQUEFACTION

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ABSTRACT

We have briefly explored the use of dispersed catalysts for conversion of an Illinois #6 into soluble products. We compared both supported and non-supported catalysts and found that the non-supported catalysts gives superior conversions. The non-supported catalysts were impregrated into the coal by use of either aqueous metal salts or organic solutions of organometallic complexes. The organometallic precursors were found to be exceptionally active and provide the greatest yields of toluene soluble products. Our key to effective dispersed catalysts is the use of a soluble sulfido complex that does not require high temperature activation.

INTRODUCTION

Although great progress has been made in converting coal to distillable liquids in high yields, the products are still not competitive with petroleum. A major problem is that under the severe conditions for bond-breaking during coal liquefaction, regressive reactions take place that produce char and coal liquids that are difficult to hydrotreat (1-6). For instance, phenolics are thought to polymerize into polymeric furans during the liquefaction process. In a similar manner, these coal liquids are high in nitrogen heterocycles. These heterocyclic oxygen and nitrogen containing molecules make coal liquids difficult to upgrade. In order to hydrotreat these materials such high temperatures and hydrogen pressures are required, that the valuable aromatic containing materials in the coal liquid are concurrently hydrogenated. In past work, we have concentrated on developing highly dispersed highly active catalysts to hydrotreat these coal liquids with the minimum consumption of hydrogen (7-11). In this work we look at the feasibility of using similar techniques to impregnate the coal with highly dispersed catalysts for improved liquefaction that give less regressive reactions.

Dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen donating solvent. An added advantage to these catalysts is that they can promote certain bond cleavage reactions during the liquefaction step. If they can aid in removing the heteroatoms, namely oxygen and nitrogen, during the early stages in coal liquefaction, then the detrimental regressive reactions would be minimized. Thus a better quality coal liquid product would be produced that would be easier and less expensive to hydrotreat.

Many workers have investigated non-supported high dispersion catalysts (12-21). Most work on dispersed catalysts has focused on metal salts such as ammonium molybdate or iron

sulfides, or oil soluble catalysts such as molybdenum naphthalate. Derbyshire et al. have conducted considerable research utilizing the $(NH_4)_2MoO_4$ and $(NH_4)_2MoS_4$ aqueous impregnation methods at low temperatures where they have shown that these dispersed catalysts can effectively utilize hydrogen to aid in subsequent conversions(13-15). The problem with most dispersed catalysts that have been tested is that they are only activated at high temperatures. For instance, molybdenum tetrathiolate decomposes to MoS_3 at low temperatures. However, the more active form is MoS_2 which is formed at much higher temperatures ($\geq 350°C$) (22,23). In a similar manner, the molybdenum naphthalate needs to be transformed into MoS_2. The importance of the correct stoichiometry has been emphasized by Montano et al. (24,25). They have suggested in work on iron sulfide catalysts that the pyrite (FeS_2) must be transformed to pyrrhotite, $Fe_{1-x}S$, ($0<x<0.125$) before it is catalytically active. Under coal liquefaction conditions, the sulfur must diffuse out of the pyrite to allow the transformation to occur. In contrast, when the precurssor is $Fe(CO)_5$, sulfur diffuses into the iron to form highly dispersed pyrrhotite.

Since we have been successful in increasing the activities of hydrotreating catalysts by use of organometallic precursors to form highly dispersed catalysts, we are very interested in using these same techniques for direct liquefaction catalysis (7-11). Our goals are to synthesize and test soluble complexes that are as close to the correct stoichiometry and structure of the active catalyst during the coal liquefaction. Thus we hope that our catalysts, since they do not require high temperature activation, will cause bond breaking reactions at lower temperatures than are currently possible with dispersed catalysts, and may therefore aid in reducing regressive reactions.

EXPERIMENTAL

The procedure for converting coal in tetralin is as follows. For the experiments involving aqueous pretreatment, the coal was pretreated by placing approximately 5 g of coal, 0.003 moles catalyst and 10 mL of distilled water in a 45-mL Parr bomb with a Teflon insert. The reactor was purged and pressurized with 500 psi of nitrogen and inserted into a preheated furnace for 30 min at 250°C. After the reactor had cooled, the insert was removed, and transferred into a centrifuge tube fitted with a screw cap. The aqueous layer was removed after centrifuging the mixture, and the pretreated coal washed twice with distilled water. The wet coal was mixed with 30 g of tetralin and then transferred to a 300 mL Autoclave Engineers Magnedrive autoclave.

All operations were conducted either in a nitrogen-filled glove bag or under a blanket of nitrogen, although brief exposure of the pretreated coal to air during the transfer could not be avoided. The autoclave was then purged and pressurized with 500 psi of hydrogen and heated at 400°C. The electric furnace could be raised or lowered by use of a remotely controled jack. The typical heat-up time was 30 min. After 20 min reaction the heater was immediately lowered. The removal of the furnace gave a rapid cool down of about 100°C in about 5 minutes. After the reaction had cooled, the coal liquid and residue were taken up in tetrahydrofuran (THF). The THF was removed under reduced pressure and the residue taken up in toluene. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The toluene and residual tetralin were then removed from the TS under reduced pressure. The TS and TI fractions were then dried at 76°C for 12 h under vacuum (< 0.1 mm).

RESULTS AND DISCUSSION

This work was conducted in order to demonstrate that there is a correlation between our hydrogenolysis results and our liquefaction results due to the means of catalyst preparation. We feel the development of hydrotreating catalysts as important, since a good hydrogenolysis catalyst, should also be a good coal liquefaction catalyst. We have prepared these highly dispersed catalysts by impregnating homogeneous organometallic complexes on the support. The advantage of these

methods are that one can create "surface confined" highly dispersed, small particle sized catalysts throughout the support. In contrast, the conventional incipient wetness technique tends to cause large metal clusters to be formed, leaving a low surface area of active catalyst, and thus much less activities.

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The coal liquefaction experiments were conducted with a high ratio of tetralin to coal (6 to 1). Therefore, we would expect that the effect of the catalyst in terms of providing a reducing environment or forming an active solvent should be minimized. Thus, any differences we see in conversions should primarily reflect the effect of the catalyst promoting bond breaking reactions. (although one could argue that the catalyst is producing low concentrations of reactants derived from the solvent that are actually producing the bond breaking).

Table 2 lists some of our results for conversion of coal into toluene soluble material. The conversion is calculated from the insoluble material corrected for the ash content. Molybdenum tetrathiolate was chosen since it is an excellent hydrogenation and liquefaction catalyst precursor and also can be used to form mixed metal sulfide clusters which may be used as hydrogenolysis catalysts. One question to be addressed for the water soluble molybdenum salt was the optimum method of preparation. We thought that the ideal way to impregnate the coal is the mix the coal in an aqueous solution of the thiomolybdate salt, and heat the solution at 250°C for 30 min. This hot aqueous impregation is thought to swell the coal, and thus allow better impregnation with the aqueous catalyst. Experiments 1-3 in Table 2 show the results after this aqueous impregnation. In the first experiment, the coal was impregnated and then dried under vacuum at 76°C to remove the water. In the second experiment, the coal was impregnated, centrifuged to remove the excess water, and the immediately placed in the autoclave. In the third experiment, the molybdate salt was dissolved in 4 mL of water, and added to the coal with tetralin, without any impregnation. As shown in this table, experiment 1 gave a low conversion (41%), compared to experiments 2 and 3 (51%). When the coal was dried, the molybdenum catalyst may have become larger in cluster size or allowed crosslinking in the coal matrix to occur.

For comparison, we chose two organometallic molybdenum dimers. A sulfido complex, $Cp_2Mo_2(\mu-SH)_2(\mu-S)_2$, and a molybdenum acetate dimer, $Mo_2(OAc)_4$. As shown in experiments 4 and 5, respectively, the sulfido dimer provides a much higher conversion than the aqueous impregnation methods, (61% compared to ≈ 50%), and also a higher conversion than the non-sulfided $Mo_2(OAc)_4$ catalyst (55%).

CONCLUSIONS

We view this enhancement with the organometalic complexes as the ability to be better dispersed than the aqueous impregnation techniques, in a similar manner as demonstrated in our hydrotreating results. The highest activity with the sulfido complex, we believe, is because the catalyst was impregnated in a highly active form, and thus does not require subsequent activiation during the liquefaction step. Thus the advantages of our methods are (1) the catalyst can be readily impregnated into the coal and (2) we can design a catalyst such that it transforms directly into the correct stoichiometry for the active form of the catalyst. In future work we hope to investigate the scope of these highly active catalysts, and prepare soluble mixed metal clusters which should enhance the liquefaction of coal still further.

ACKNOWLEDGEMENTS

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Table 1

TURNOVER FREQUENCIES FOR QUINOLINE HDN[a]

Catalyst	Precursor	TF^b		
		THQ	PCH	PB
NiMo	Conv	67.4	8.2	0.3
NiMo(OM)	$Mo_2(OAc)_4$	41	3.4	0.5
NiMo(OM)	$Mo_2(allyl)_4$	111	26.5	1.4

[a]Reaction of 10 mL of 0.0197 M quinoline in n-hexadecane and 0.100 g catalyst at 350°C and 500 psig H_2.

[b]TF - moles reactant or product/total moles metal/h

Table 2

CATALYZED TETRALIN CONVERSIONS[a]

No	Pretreatment	$\% TS^b$
1	$MoS_4/Dried^c$	41
2	$MoS_4/4\ mL^d$	52
3	MoS_4/Wet^e	52
4	$Cp_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$	61
5	$Mo_2(OAc)_4$	56

[a]Reaction conducted in 300-mL autoclave of 5 g coal in 30 g of tetralin and 500 psi H_2 at 400°C/20 min.
[b]Solubility based on wt % insoluble material, corrected for ash.
[c]Coal was dried at 76°C under vacuum after aqueous molybdenum impregnation.
[d]Molybdenum was dissolved in water (4 mL) added to the coal/tetralin mixture.
[e]Coal was impregnated with aqueous molybdenum, and transferred to the autoclave while wet.

REACTIVE INTERMEDIATES IN CATALYTIC COPROCESSING

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INTRODUCTION

Fundamental studies of the mechanism of catalytic coal con-
version not only provide an understanding of how current cata-
lysts work but also offer the prospect of designing better cata-
lysts in the future. One approach to the study of catalysis is to
observe the production of products from single, known probe com-
pounds. This approach is especially useful when the products can
be shown to arise only from particular reactive intermediates,
such as cations or radicals.

Three probes were used to investigate the mechanism of
catalysis of a dispersed molybdenum sulfide catalyst. The 1,5-
dimethylnaphthalene (1,5-DMN) was selected because of its ability
to distinguish three important types of reactions (Figure 1).
Under cationic conditions, the methyl groups of 1,5-DMN migrate
to form 1,6-DMN and subsequently 2,6-DMN.[1] Each isomer will react
to give an equilibrium mixture of all three isomers, but the 1,5-
DMN is the least stable and thus is the most sensitive probe for
a cationic environment. The 1,5-DMN can also undergo demethyla-
tion to form 1-methylnaphthalene (1-MN). This reaction can be
envisioned as occurring either via a cationic cracking mechanism
or via an ipso substitution by a hydrogen atom; however, the evi-
dence given below supports a radical ipso substitution under our
conditions. The third reaction of 1,5-DMN is hydrogenation. This
leads to the formation of 1,5-dimethyltetralin (1,5-DMT). Thus,
three reaction types of interest in catalytic coal conversion are
distinguished by this probe. In addition, decalin and tricyclo-
decane (Figure 2) were used to distinguish hydrogen abstraction
reactions. The results obtained from these three probes provide a
description of the reaction environment present during catalytic
coprocessing.

Other workers at the PETC[2] have shown molybdenum trisulfide
prepared by the method of Eggertsen and Roberts[3] to be an effec-
tive coprocessing catalyst. Reactions of the probe compounds in
the presence of this catalyst were compared to the reactions
observed in the presence of a known cationic catalyst and a known
radical initiator. These reference additives were selected to
ensure that the probes would indeed distinguish the different
reaction environments. Bibenzyl generates free radicals by a
thermolytic dissociation to form stoichiometric amounts of benzyl

radicals.[4] These radicals abstract hydrogen from solvent and solute, and thus provide a pool of radicals of varying activity. Benzyl radicals also abstract hydrogen atoms from gas phase hydrogen, producing hydrogen-atom-mediated hydrocracking.[4] A commercial cracking catalyst (D980-13) was selected because of the known acidic character of silica-alumina catalysts.[5] Thus, a comparison of the reactions of the probes in the presence of the molybdenum sulfide with the reactions in the presence of the reference additives provides information about the reaction environment generated by the coprocessing catalyst.

EXPERIMENTAL

The commercial silica alumina (D980-13) was obtained from W.R. Grace (grade 980-13, 13% alumina) as an extrudate. The friable solid was ground with a mortar and pestle, and oven-dried at 150°C overnight. The molybdenum trisulfide was prepared from ammonium tetrathiomolybdate by precipitation from an aqueous solution using formic acid.[3] This procedure is best carried out in a hood because of the hydrogen sulfide formed.

All reactions were performed using 40-mL 316-stainless steel reactors. The 8-gram reaction mixtures contained the probe (200 mg); a silica-alumina (10 mg), molybdenum trisulfide (10 mg), or bibenzyl (2.0 g) additive; and n-octacosane solvent. The reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and shaken at temperature for 60 minutes. The products were washed from the cooled reactor using inhibitor-free tetrahydrofuran (Aldrich 27,038-5) and were analyzed by GC-MS.

RESULTS

The reactions of 1,5-DMN are shown in Figure 1. The amounts of the products obtained in the presence and absence of the three additives are given in Table I. The effect of the added bibenzyl is to increase the yield of 1-MN because of the increased production of hydrogen atoms.[4] Significantly, no isomerization of the methyl groups is seen in the blank or in the presence of the free radical initiator, nor is the hydrogenation to 1,5-DMT an important reaction under these conditions. In the presence of the acidic catalyst, D980-13, the isomerization of the methyl groups becomes the predominate reaction. Of the recovered dimethylnaphthalenes, 83% have at least one methyl group in a beta position. The 1,5-DMN is indeed sensitive to the presence of the acidic sites of this catalyst. Both 1-MN and 2-MN are obtained as the demethylated products. The total amount of demethylation is the same as was seen in the absence of catalyst, about 10%. In this case, it is reasonable to assume that the cationic mechanism is superimposed on the background radical reaction. The

1,5-DMN can rearrange via a cationic mechanism, and the isomers thus produced can subsequently crack by a hydrogen atom mechanism. In addition, the 1-MN and 2-MN formed from the cracking can be interconverted by the acid catalyst. Again, no effect is seen on the amount of hydrogenation, which remains low. The results obtained in the presence of the molybdenum trisulfide catalyst are shown in the last column of Table I. Molybdenum disulfide is assumed to be the actual form of the catalyst under liquefaction-like conditions.[3] The effect of adding this catalyst is to increase the extent of hydrogenation to form the dimethyltetralin. The molybdenum catalyst does not exhibit cationic behavior, as evidenced by the lack of isomerization of the methyl groups, nor does it increase the extent of hydrocracking to form methylnaphthalene. The lack of cationic activity was initially surprising because single crystal experiments at lower temperatures have associated carbonium ion intermediates with the basal plane of molybdenum disulfide.[6] However, a similar lack of isomerization has been noted during the cracking of 1-methylnaphthalene in the presence of a supported CoMo catalyst at slightly higher temperatures.[7]

In addition to the aromatic hydrocarbon probe, two alicyclic hydrocarbons, decalin and tricyclo[5.2.1.0^{2,6}]decane (TCD), were used as probes (Figure 2). The isomerization of cis- to trans-decalin requires the removal of a tertiary hydrogen, whereas the isomerization of endo- to exo-TCD requires the removal of a secondary hydrogen.[8] The ratios of the isomers (more stable / less stable) after reaction in the presence and absence of the three additives are given in Table II. The effect of added bibenzyl is to increase the extent of isomerization of both probes. The radical isomerization of the decalin is known to occur under these conditions,[9] but the radical isomerization of the TCD was surprising. In general, Wagner-Meerwein rearrangements are not observed for radicals. One exception is the recently reported radical isomerization of homoadamantane to methyladamantane.[10] The addition of the D980-13 acidic catalyst had no effect on the isomerization of the TCD, but it did cause an increase in the extent of the isomerization of the decalin. Apparently the decalin can isomerize by either hydrogen atom or hydride abstraction. The results obtained from the molybdenum sulfide are very similar to the results from the D980-13 catalyst for this set of probes. The isomerization of the TCD is unaffected, but the isomerization of the decalin is accelerated.

DISCUSSION

The results obtained from the three probes are summarized in Table III. The catalysts are considered to either promote (+) or not promote (-) the reactions listed. Aromatic methyl group hydrocracking is promoted only by bibenzyl and is thus proceeding via an ipso substitution by a hydrogen atom.[4] The lack of crack-

ing in the presence of the D980-13 catalyst is likely due to the difficult formation of methyl cations. The isomerization of endo-TCD is also catalyzed only by the bibenzyl and is therefore proceeding via a radical hydrogen abstraction from a secondary carbon. If free radicals are formed in the presence of the molybdenum sulfide, they are not energetic enough to react with gas phase hydrogen to form the hydrogen atoms, nor are they energetic enough to abstract the secondary hydrogen from the TCD. This means they have to be considerably less reactive than the benzyl radicals formed from the bibenzyl.

Since the isomerization of the 1,5-DMN is catalyzed only by the D980-13 acidic catalyst, it is probably proceeding via a cationic mechanism similar to that found in the presence of solution phase acids.[1] The absence of this isomerization for the molybdenum sulfide indicates either that there are few acid sites of sufficient strength to catalyze the isomerization, or that the active sites are not accessible to the 1,5-DMN. Other sites of lower acidity may be present.

All three additives are capable of increasing the amount of isomerization of decalin. At least two mechanisms are operative. In the presence of a radical initiator, the isomerization is driven by the abstraction of a hydrogen atom from the tertiary carbon. In the presence of the acid catalyst, a similar mechanism involving hydride abstraction would account for the increased isomerization. Isomerization occurs also in the presence of the molybdenum sulfide. Since the molybdenum catalyst shows no activity in the other radical and cationic reactions above, it may be catalyzing the isomerization by yet a third mechanism. Dehydrogenation of the cis-decalin by loss of one tertiary hydrogen and an adjacent secondary hydrogen leads to an octalin with the double bond to the bridgehead carbon. Subsequent hydrogenation from the opposite side leads to the trans-decalin. The feasibility of a dehydrogenation – hydrogenation mechanism is strengthened by the observed hydrogenation activity described next.

Only the molybdenum sulfide was effective in hydrogenating the naphthalene ring to form tetralin. The absence of concomitant radical or cationic reactions indicates that the hydrogenation is probably proceeding via a surface-bound intermediate or a concerted addition of hydrogen. Based on the information provided by these probes, the effectiveness of the molybdenum sulfide catalyst in coprocessing may lie in the fact that it provides hydrogenation activity but does not introduce strong acid sites associated with coke formation nor does it promote radical formation, which has been associated with retrogressive reactions. The possible presence of weaker acid sites, capable of cracking other alkyl chains, is being investigated.

CONCLUSIONS

Probe compounds have been used to explore the mechanism of catalysis of a molybdenum sulfide known to be active for the co-processing of coal and oil residua. Under typical coprocessing conditions, the sulfide displayed predominately hydrogenation activity. Comparison with additives known to be sources of radical and cationic activity provided no evidence that the molybdenum catalyst has either of these properties.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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TABLE I. Normalized Distribution of Products from 1,5-Dimethyl-naphthalene.

|		ADDITIVE		
	None	Bibenzyl	D980-13	MoS_3
1,5-DMN	83%	48%	15%	66%
1,6-DMN	1%	1%	38%	3%
2,6-DMN	0	1%	33%	0
1-MN	13%	38%	6%	14%
2-MN	0	1%	8%	0
NAP	0	8%	0	1
DMT	4%	2%	0	17%

Note: DMN = Dimethylnaphthalene
      MN = Methylnaphthalene
      NAP = Naphthalene
      DMT = Dimethyltetralin

TABLE II. Comparison of the Extent of Isomerization of cis-Decalin and endo-Tricyclo[5.2.1.0^{2,6}]decane.
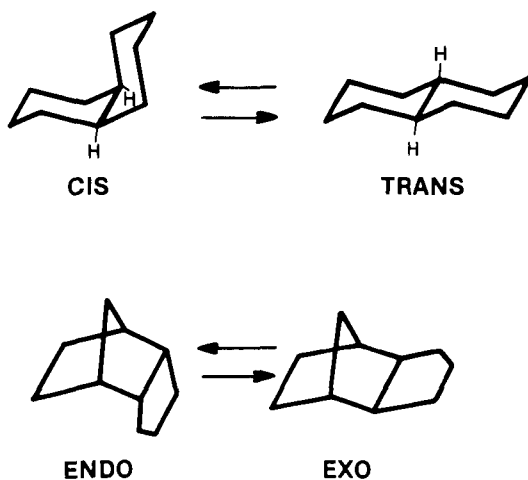
CATALYST	TCD EXO / ENDO	DECALIN TRANS / CIS
None	0.31	0.29
Bibenzyl	1.38	2.33
D980-13	0.33	0.91
MoS_3	0.28	1.13

TABLE III. Summary of Probe Reactions.

	Bibenzyl	D980-13	MoS_3
Methyl-Group Hydrocracking	+	-	-
Isomerization at 2° Carbon	+	-	-
Isomerization of Aromatic Alkyl-Group	-	+	-
Isomerization at 3° Carbon	+	+	+
Hydrogenation	-	-	+
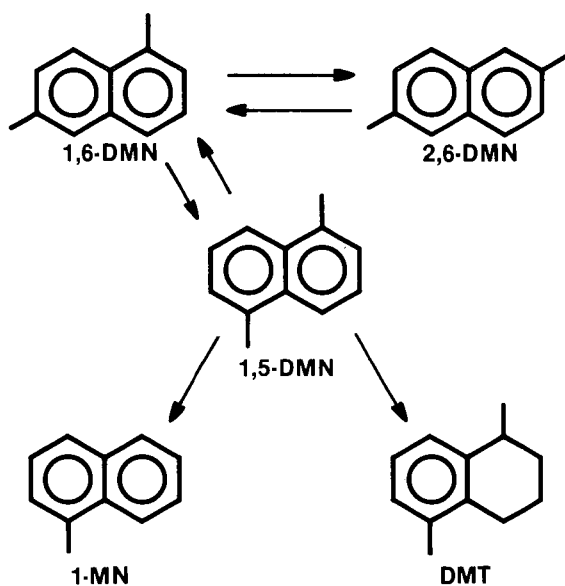
FIGURE 1.   REACTIONS OF 1,5-DIMETHYLNAPHTHALENE.

NOJ18,558

FIGURE 2.   THE ISOMERIZATION OF DECALIN AND
TRICYCLO[5.2.1.0^{2,6}]DECANE.